R004-C
Renewable Oil Refinery Development for Commercialization
Submitted by Energy & Environmental Research Center
Principal Investigators: Chad A. Wocken
Request for $500,000; Total Project Costs $1,000,000

Energy & Environmental Research Center (EERC) Response to Independent Technical Review Comments

Reviewer concern: Insufficient description of technology

EERC response: The proposed EERC-developed technology converts renewable oil feedstocks to fully fungible, oxygen-free fuels and hydrocarbon products that are essentially identical to their petroleum-derived counterparts. The technology comprises a series of primary unit operations including:

1. Hydrodeoxygenation (HDO) to convert renewable oils to straight-chain hydrocarbons.
2. Degassing and water removal to ensure against water contamination of next-stage isomerization/cracking processing.
3. Isomerization and cracking to achieve a jet fuel specification-compliant mix of branched hydrocarbons.
4. Distillation to yield jet fuel, naphtha (a light hydrocarbon mix used as feedstock for chemicals and gasoline), and diesel fuel.

Based on discussions between EERC researchers and Tesoro Mandan Refinery personnel, process conditions utilized to conduct the above operations are within the range typical of petroleum refinery unit operations. The EERC has developed and applied for patent protection on intellectual property (IP) utilized in Operations 1, 3, and 4. Work performed to date under an EERC contract with the Defense Advanced Research Programs Agency (DARPA) has focused on jet fuel production, which is why the proposed scope of work will also encompass diesel fuel and naphtha production and evaluation. Analysis of EERC jet fuel samples has been conducted by the U.S. Air Force Research Lab at Wright-Patterson Air Force Base. A summary of military jet fuel (JP-8) specification test results is provided in Table 1. A gas chromatograph (GC) of EERC renewable JP-8 is compared to typical petroleum-derived JP-8 in Figure 1.

Reviewer concern: Insufficient detail on technology optimization objectives and execution

EERC response: Process optimization work will be focused on improving the overall efficiency of the renewable feedstock-refining process to ensure its economic competitiveness with petroleum refining. Optimization work will be conducted with oil from crambe and at least one other North Dakota oil seed. With each feedstock oil, optimization testing will focus on maximizing the conversion of feedstock to diesel fuel via identification of best catalyst and operational conditions including temperature, pressure, hydrogen concentration and flow rate, and residence time in the reactor. Following optimization of a diesel fuel process, conditions will be developed for achievement of maximum jet fuel yield. Data generated during the optimization of both processes will be provided to Unifield Engineering to support development of a pilot

Table 1. JP-8 Specification Analysis of EERC Renewable Jet Fuels

ID	Specification Requirements	Typical JP-8	Coconut/Soy	Waste Grease	2 Gallon Canola	25 Gallon Canola
Submitted			Jan 08	May 08	Nov 08	Dec 08
Flash	≥ 38°C	51°C	49°C	46°C	46°C	46°C
Freeze	≤–47°C	–50°C	–52°C	–49°C	–53°C	–55°C
n-paraffins	No req'mt	18%	32%	23%	16%	16%
i-paraffins	No req'mt	42%	17%	44%	~66%	~66%
c-paraffins	No req'mt	21%	31%	26%	<1%	<1%
Aromatics	≤ 25%	19%	20%	7%	17%	17%
Density	≥ 775 kg/m3	804 kg/m3	805 kg/m3	786 kg/m3	784 kg/m3	787 kg/m3
Net Heat	≥ 42.8 MJ/kg	43.3 MJ/kg	42.9 MJ/kg	43.6 MJ/kg	43.5 MJ/kg	43.4 MJ/kg

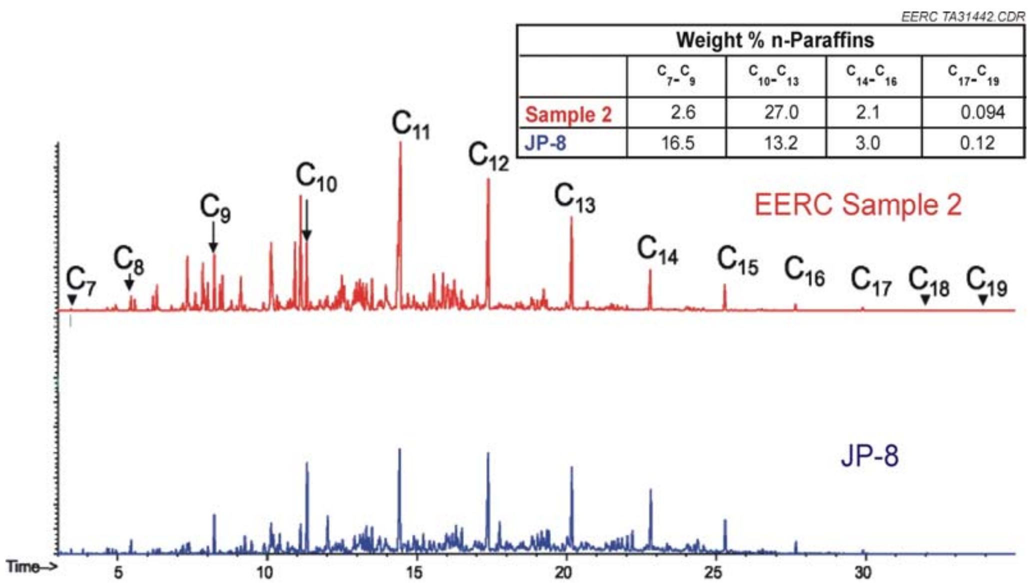

Figure 1. GC of EERC renewable JP-8 compared to petroleum-derived JP-8.

plant design with the flexibility to produce either primarily diesel or jet fuel in response to market demand.

Reviewer concern: Cost-share availability

EERC response: As proposed, cost share was to be provided from the U.S. Department of Energy-sponsored EERC Center for Biomass Utilization (CBU) Program. In addition to this proposed source of cost share, recent developments at the EERC have resulted in the certain and immediate availability of the necessary cost-share funding from the U.S. Department of Defense-sponsored EERC Advanced Tactical Fuels Program.

Reviewer concern: Viability of crambe oil as feedstock

EERC response: The hypothesis supporting crambe oil as a viable feedstock is based on recent EERC experience producing jet fuel from feedstock containing predominantly C-18 fatty acid chains. Crude hydrocarbon produced via EERC technology using soy and canola oils possesses a variety of carbon chain lengths with the greatest concentration centered on C12. This distribution is ideally suited for jet fuel. Diesel fuel typically contains a slightly longer carbon chain distribution ranging from C12–C22. Crambe oil, with 45%–60% C22 is likely to provide the carbon chain length needed to meet the full distillation profile of petroleum-derived diesel.

Commercially and economically, crambe is interesting because of its exceptional yield and oil-content performance throughout North Dakota, and especially in the southwestern quadrant. This region of North Dakota and bordering states currently lacks rotational crops compatible with traditional grass crops of wheat and barley. Additionally, there are no broad-leaf or energy crops which can be grown competitively in this region. Crambe was commercialized in the early 1990s, reaching a peak production of 60,000 acres. The crop was grown primarily to satisfy the erucic acid market in Europe until subsidies for European producers shifted to support high erucic acid rapeseed. Data from several years' worth of production is available through the North Dakota State University Carrington Research Extension Center (CREC), illustrating the advantages of crambe for cool and dry climates. Further, the input costs for production are among the lowest of all crops grown in North Dakota and suggest that oil could be produced for $0.20–0.30/lb at seed prices attractive to producers.

Reviewer concern: Tesoro and 3M interest and commitment

EERC response: Following a year of record prices for petroleum and commodities, investors are cautious about new biofuel technology. The EERC, through its contract with DARPA, has demonstrated the technical feasibility and preliminary economic viability of producing fully fungible fuels made from renewable feedstock that are indistinguishable from their petroleum-derived counterparts. The objective of the proposed project is to advance the research and conduct the necessary process design to allow for a detailed assessment of the economic viability of EERC renewable oil-refining technology. Financial support of this effort will provide the design and economic data that industry partners like Tesoro and 3M need to make business decisions and investments. Successful completion of the proposed effort will allow Tesoro to take an active role in hosting, operating and demonstrating a renewable oil refinery at the facility in Mandan, North Dakota. A letter of commitment from Tesoro is being submitted along with this response-to-comments, which outlines its desired role in furthering commercialization of renewable fuels. 3M commitment to the project lies in evaluating naphtha for petrochemical projects. Renewable naphtha produced from the proposed effort will be submitted to 3M for its evaluation. Pending successful evaluation by 3M, additional financial and commercialization support will be forthcoming along with its ability to generate a market for renewable oil chemical intermediates.

Reviewer concern: Investigators' qualifications and awareness of current related research activity

EERC response: Chad Wocken, proposed project manager, and Ted Aulich and Paul Pansegrau, key project personnel, have devoted approximately 50% of their working hours over the last 30 months to developing an energy-efficient process for conversion of renewable oils to jet fuel, with the objective of commercializing the process to supply specification-compliant jet fuel to the U.S. military. This DARPA-funded research effort was centered on a technology pathway developed by the EERC based on a comprehensive literature and patent search, and it led to the EERC renewable jet fuel process, which has been validated via the U.S. Air Force Research Laboratory analysis of jet fuels produced by the EERC from a variety of feedstocks. A key DARPA requirement was a plan to commercialize the jet fuel technology, and a key project conclusion was that like petroleum refining, renewable oil refining requires complete feedstock utilization and generation of a slate of products to achieve commercial viability. The work proposed here is focused on establishing the optimal-efficiency operational requirements for producing not only jet fuel, but also diesel fuel, naphtha, and possibly other products, thereby ensuring the best (most economic) feedstock utilization.

The above-mentioned researchers are aware of ongoing research and commercialization activities in renewable oil refining and maintain their awareness by working with the competition. The EERC actively cooperates with two key competitors, UOP (Honeywell) and Syntroleum, in providing fuel property data to the American Society of Testing and Materials (ASTM) and the Commercial Alternative Aviation Fuels Initiative (CAAFI), with the objective of developing a plan for qualifying renewable jet fuel for use in military and commercial aircraft. The EERC has also explored collaboration possibilities with Neste Oil, another key competitor, and learned about important similarities and differences between the EERC and Neste refining technologies. Key to both the technical and economic success of any oil (renewable or petroleum)-refining technology is the right catalyst, and the EERC is partnered with major international catalyst producer Albemarle for catalyst supply. As a successful competitor in the catalyst business, Albemarle is acutely aware of what is needed to ensure freedom to operate in commercial fuel processing and is committed to providing the EERC with the most technically, economically, and legally viable catalyst technology.

Reviewer concern: Insufficient description of management plan communication scenario

EERC response: Upon commencement of a funded project, a kickoff meeting will be held at the EERC to discuss roles, budget, and time line. At that time, a lead engineer from Unifield will be selected as the point of contact for design activities. It is anticipated that in the first 6 weeks of the project, a series of information exchanges would take place between the EERC and Unifield in which detailed operational data would be passed from the EERC to Unifield. Operational data, preliminary design parameters, process modeling data, and other pertinent information developed under previous efforts will be submitted to Unifield to support technology scale-up and design. Following review of this information, Unifield will develop a data needs table. The data needs table will form the basis for subsequent engineering support and testing by the EERC.

Monthly progress meetings will be held via teleconference and will include representatives from Unifield, Tesoro, and the EERC. In addition to the monthly meetings, it is anticipated that one meeting will be held at Unifield's office in either Billings or Bismarck, one meeting at the Tesoro Mandan Refinery, and one meeting at the EERC. Quarterly teleconference meetings and at least two on-site meetings will be held with 3M.

Although not quantified with a formal budget, significant participation is expected from Tesoro and 3M in their efforts to evaluate the merit of EERC technology and to support technology development. Their participation and associated in-kind cost share is critical to fulfilling the objectives of the project and advancing deployment of a commercially viable technology.

Reviewer concern: Equipment purchase not adequately justified

EERC response: No equipment purchase is planned or anticipated.

Reviewer concern: Insufficient facilities and equipment description

EERC response: The EERC houses a number of continuous and batch reactors for processing liquids or slurries at high temperatures and pressures. A summary of reactor systems available for the proposed effort follows. Typical reactions carried out in the facility include hydrogenation, green diesel production, distillate fuel upgrading, and coal liquefaction. A dedicated 12-liter batch distillation system, GC–mass spectrometer (MS), and GC-thermal conductivity detector (TCD) are available for upgrading and testing all liquid products, as are various units of specialized equipment for testing fuel performance parameters.

LIQUID PROCESSING SYSTEMS

Continuous reactors:
- Small continuous reactor (SCR)
- Large continuous reactor (LCR)
- Continuous tubular reactor (CTR)

Batch Reactors:
- 250-cc reactor (PR-250)
- 500-cc reactor (PR-500)
- 1-L reactor (PR-1L)
- 1-gallon reactor (R1G)
- 2-gallon reactor (R2G)

SCR

The SCR is a 50–500-cc/hr, vertically oriented plug-flow reactor designed and utilized to carry out two-phase gas/liquid reactions over solid catalysts on the bench scale. It is used primarily for exploratory research or small-scale liquid processing. The reactor body is constructed of type 316 stainless steel and is fully enclosed in a single-zone electric clamshell heater. The SCR has been tested to temperatures of 600°C and pressures of 1000 psig. All temperatures, pressures, and flow rates are computer-controlled and monitored from behind an explosion-rated blast wall.

Reactions tested to date in the SCR include the following:

- Crop oil and fatty acid conversion to distillate fuels
- Distillate fuel hydrocracking and hydrotreating
- Paraffin reforming to aromatics under mixed atmospheres
- Alcohol upgrading

LCR

The LCR is a vertically oriented tubular reactor designed for large liquid throughputs with short residence times and high pressures. It is used primarily for reforming of liquid fuels and alcohols to produce high-pressure hydrogen on demand. It has also been used in the production of renewable distillate fuels from vegetable oils.

Two liquid streams can be simultaneously fed to the LCR. Liquid flow is controlled by Hydro-Pac pumps with discharge pressures of up to 15,000 psig and flow rates ranging from less than 0.1 gal/hr (0.25 Lph) up to 24 gal/hr (91 Lph) at maximum pressure. The LCR is capable of operating at temperatures of 1200°F (649°C) and pressures up to 12,000 psig. Multiple reactor beds of different sizes and proportions are installed for use in series or parallel flow. A pressurized CO_2 trap allows for hydrogen separation during liquid fuel reforming. Volatile products are collected in a chilled condenser, and a slipstream of dry gaseous product is sampled for online analysis. Prior to venting, the dry product gas stream is depressurized and combusted in a thermal oxidizer.

CTR

The CTR is a vertically oriented two-bed Autoclave reactor system with multiple independently heated zones. This reactor was built primarily for processing and upgrading distillate fuels and vegetable oils in green diesel production. It has successfully produced barrel quantities of renewable distillate fuel from crop oils.

The CTR can be run at conditions up to 950°F (500°C) and 5000 psig at liquid flow rates from less than 0.5 lb/hr up to tens of pounds per hour. Gas flow rate can be metered by a mass flow controller up to 100 scfh (47 slpm).

Batch Autoclaves

The EERC houses a number of batch autoclave systems ranging in size from 250 cc up to 2 gallons. These reactors are used when very high pressures are required or when the feed is a solid or slurry. The reactors, ranging in size from 250 cc to 1 liter, can be used at pressures and temperatures up to 5000 psig and 932°F (500°C). The 1-gallon autoclave is rated to 5100 psig and 950°F (510°C), and the 2-gallon autoclave is rated to 5500 psig and 650°F (340°C).

The 1- and 2-gallon reactors are equipped with heaters, gas fill and vent lines, and a vacuum pump to assist in venting or to run reactions at below atmospheric pressure. Vent lines run to a water-cooled condenser for collecting volatile product. The 2-gallon autoclave is heated in four separate bands to help maintain constant temperature throughout. This reactor is stirred by a belt-driven water-cooled mixer with two propellers and an impeller along the shaft length. The 1-gallon autoclave is heated by a single zone heater. The 1-gallon reactor can be run with or without a mixer and is equipped with a bottom drain for liquid removal. Both reactors are equipped with thermocouples at the top and bottom for monitoring the temperature of both the vapor and liquid phases.

Analytical work will be performed at the EERC and, when necessary, contract laboratories to evaluate product chemical composition and physical properties. The EERC has in-house gas and liquid chromatography capabilities for detailed compositional analysis of feedstocks, fuels, and other products, and the ability to conduct real-time gas analysis on continuous reactor systems. Fuel property tests to be conducted at EERC laboratories include freeze point, flash point, density, heat of combustion, acid number, and water content.

Reviewer concern: Budget allocation

EERC response: Although the $300,000 subcontract to UniField is not cost-shared with cash, Tesoro will provide significant in-kind support to UniField through evaluating options for integrating renewable oil-refining operations with operations at the Mandan refinery and assisting with unit operation designs. Assuming success in the proposed project, Tesoro's willingness to host and operate a 0.5–5-million-gallon/year renewable oil refinery will be of major value.

Reviewer concern: Need for detailed economic evaluation

EERC response: A detailed economic assessment will be critical to subsequent commercialization efforts. However, capital equipment and operating costs for a full-scale commercial plant cannot be accurately determined at the current development stage of the technology. Utilizing the data generated from the proposed effort and the capital equipment cost for the pilot plant, the EERC will work with Unifield and Tesoro to estimate commercial plant economics. At the conclusion of this project and following subsequent pilot plant operation, a revised estimate of commercial plant economics can be conducted along with a detailed commercial plant design.